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Abstract

The size distribution of polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives was determined during the intensive sampling campaigns of the POVA (POllution des Vallées Alpines) research program, in two French alpine valleys, in winter and summer. The size distributions of PAHs, oxygenated PAHs (OPAHs) and nitrated PAHs (NPAHs) present large variations with year time and site type (traffic; suburban and rural). In general, these compounds were mainly associated (60-90%) with fine particles (D_p < 1.3 µm) in agreement with their release from sources (primary and/or secondary). The pollutant distributions with particle size were unimodal and centred at 0.85 µm both in the Chamonix and Maurienne valleys. The summer size distribution of NPAHs was centred at D_p = 2.75 µm. PAH, OPAH and NPAH super micrometer fractions were significantly larger in summer for most sites suggesting the existence of a second mode in that particle size range. A possible reason to explain this phenomenon is that aerosol was locally polluted and characterised by fine particles in winter whereas in summer, aerosol was more mixed and older with possibilities of adsorption of gaseous organic compounds at the surface of the pre-exiting particles. In summer, NPAHs were associated to a greater degree with the super micrometer fraction of the aerosol than the other categories of compounds.

Keywords: Polycyclic aromatic hydrocarbons; Nitrated polycyclic aromatic hydrocarbons; Oxygenated polycyclic aromatic hydrocarbons; Size distribution; Atmospheric pollution; POVA (POllution des Vallées Alpines); Alpine valleys

1. Introduction and objectives

Till now, only, few studies have focused on the size distribution of the polycyclic aromatic hydrocarbon (PAH) oxidation products, namely oxygenated PAHs (OPAHs) and nitrated PAHs (NPAHs). PAHs are emitted directly from combustions whereas NPAHs and OPAHs are both primary emitted and secondarily formed in the atmosphere, by action of oxidants (OH, NO_3, O_3) (Arey et al., 1986; Atkinson et al., 1989; Atkinson et al., 1990; Barbas et al., 1996; Environmental Health Criteria (EHC) 229, 2003; Helmig and Harger, 1994; Perraudin et al., 2007; Sasaki et al., 1997). PAH derivatives (NPAHs and OPAHs) have been recognised as direct-acting mutagens and carcinogens making them more toxic than their parent PAHs which require the enzymatic activation of their properties (Durant et al., 1996; Durant et al., 1998; Hannigan et al., 1998; Lewtas et al., 1990; Pedersen et al., 2004; Pedersen et al., 2005; Schuetzle, 1983). Particle size distribution of these mutagenic compounds is very important when assessing the influence on human health, because the particle size controls deposition behaviour of particulate matter in the respiratory organs. Coarse particles mainly deposit in the anterior nasal region and the main extrathoracic region. In contrast, fine particles easily reach the pulmonary alveoli.

During the last thirty years, measurements of the particle size distribution of PAHs have been performed in various locations such as Anvers (Belgium) (Van Vaeck and Van Cauwenberghe, 1978; Van Vaeck et al., 1979), Los Angeles, Claremont, Boston (USA) (Allen et al., 1996; Miguel et al., 2004; Venkataraman and Friedlander, 1994), Barcelona (Spain) (Aceves and Grimalt, 1993), or Guangzhou (China) (Bi et al., 2005). In these studies, PAHs were found predominantly associated with fine aerosols (D_p < 2.0 µm) and a similar partitioning was observed for PAHs with the molecular weight in the same range (Van Vaeck and Van Cauwenberghe, 1978; Venkataraman and Friedlander, 1994). In urban atmosphere, low MW-PAH (MW < 202 g mol^{-1}) showed a bimodal distribution between the fine (D_p < 2 µm) and the coarse aerosol (D_p > 2 µm) whereas

those with molecular weights exceeding 228 g mol^{-1} were associated primarily with the fine fraction (Allen et al., 1996). In warm periods (Miguel et al., 2004; Van Vaeck and Van Cauwenberghe, 1978; Venkataraman and Friedlander, 1994) and at sites far from emission sources (Bi et al., 2005; Van Vaeck et al., 1979), PAHs were found to partition to larger aerosols.

By contrast, few data are available on the size distributions of NPAHs and OPAHs. To the best of our knowledge, NPAH size distributions were only reported in four studies and concerned a limited number of compounds such as 1-nitropyrene, 2-nitropyrene, 2-nitrofluoranthene and dinitropyrene isomers (Cecinato et al., 1999; Hayakawa et al., 1995; Jinhui and Lee, 2000; Kawanaka et al., 2004). OPAH size distributions were only studied by Allen et al. (1997) and by Schnelle-Kreis et al., 2001).

In the frame of the POVA research program (Albinet et al., 2007a; Brulfert et al., 2005), the distribution behaviour of PAHs, OPAHs and NPAHs in the airborne particulate size fractions were investigated. Besides that, the elucidation of influence of site typology and year time onto these distributions was attempted.

2. Experimental sections

2.1. Sampling sites

The detailed description of the sampling sites are presented in a companion paper (Albinet et al., 2007a).

Briefly, two sites (C1 and C2) were located in the Chamonix valley (Cv). The first sampling site (C1) is considered as a suburban site. The second sampling site (C2) was close (< 10 m) to a national road with a large volume of traffic (> 10 000 vehicles day^{-1}) and can be classified as a traffic site.

The two others sites (M1 and M3) were located in the Maurienne valley (Mv). Site M1 can be considered as a rural site. The second sampling site (M3) can be classified as a suburban site.

2.2. Sample collection

Airborne particulates were collected using a high volume cascade impactors (Graseby Andersen, 35 m^3 h^{-1}). Sampling duration was 24 h (starting at 8:00 local time). The particles collected using this type of sampler were separated into seven size ranges: D_p < 0.39 µm (stage 7 or back up filter), 0.39-0.69 µm (stage 6), 0.69-1.3 µm (stage 5), 1.3-2.1 µm (stage 4), 2.1-4.2 µm (stage 3), 4.2-10.2 µm (stage 2) and 10.2-50 µm (stage 1). Samples were collected on six separated fritted quartz fiber filters (Tisch Environmental, 142×149 mm) and a back up quartz fiber filter (Whatman QM-A, 203×254 mm). Field blanks (ie, exposed filters without any air filtration) were collected weekly for each sampler and sampling site during both sampling campaigns. Prior to sampling, filters were burnt at 500°C for 12 h to remove any organic compounds that might be present on the filters. After collection, samples were stored at -18°C in individual glass Petri dishes (pre-washed) wrapped in aluminium foil and placed in opaque reclosable poly bags.

2.3. Sample extraction and analysis

The complete PAH, NPAH and OPAH analytical procedures and quality assurance are presented in detail elsewhere (Albinet et al., 2006; Albinet et al., 2007b). HPLC-grade quality solvents were used and purchased from Carlo Erba SDS (Peypin, France).

Filters were extracted with dichloromethane using pressurized liquid extraction. Consecutive impactor stages from the winter campaigns were extracted together (1 and 2, 3 and 4, etc) while those from the summer campaign were extracted individually, except for stages 1 and 2. All extracts

were divided into two equal fractions that were used for the determination of PAH and of NPAH and OPAH concentrations, respectively. Both fractions were evaporated under a nitrogen stream and adjusted to 1 ml with acetonitrile (for the analysis of PAHs) or dichloromethane (for the analysis of NPAHs and OPAHs). 16 PAHs were quantified by HPLC with fluorescence/UV detection (see Tables 1 and 2 plus acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene). NPAH and OPAH concentrations were determined simultaneously using gas chromatography-mass spectrometry with negative ion chemical ionization (GC/NICI-MS) and selective ion monitoring mode (SIM). The column used was a 5% phenyl-substituted methylpolysiloxane (DB-5MS, 30 m × 0.25 mm I.D., 0.25 µm film thickness, J&W Scientific, USA). The method includes a liquid chromatography purification procedure on solid phase extraction (SPE) cartridges. A total of 17 NPAHs and 8 OPAHs were quantified (see Tables 1 and 2 plus 1-nitronaphthalene, 2-nitronaphthalene, 2-nitrofluorene, 9-nitroanthracene, 9-nitrophenanthrene, 3-nitrophenanthrene; 1-naphthaldehyde, 9-fluorenone, 9-phenanthrenecarboxaldehyde, 9,10-anthraquinone).

Analytical limits of detection defined as the lowest concentration of the compound than can be detected (S/N=3) were used to calculate the methodology limits of detection for each individual compound. Individual NPAH detection limits in a typical air sample of 360 m^3 ranged between 0.01 and 0.07 pg m^{-3}. OPAH detection limits for an air sample of 360 m^3 ranged between 0.01 and 2.6 pg m^{-3}.

3. Results

3.1. Data analysis

To succinctly describe contaminant mass size distributions, geometric mean diameters (GMD) were calculated as

$$\log GMD = \frac{\sum m_i \log Dp_i}{\sum m_i} \quad (1) \qquad (1)$$

where m_i is the mass of compound in size class i and Dp_i is the geometric mean particle diameter collected on stage i. Geometric standard deviations (σ_g) were calculated as

$$(\log \sigma_g)^2 = \frac{\sum m_i (\log Dp_i - \log GMD)^2}{\sum m_i} \qquad (2)$$

using GMD as defined above.

Size distributions were plotted by normalizing the compound concentrations for each stage to the total compound concentration and the logarithmic bin width. The data are represented as $\Delta C/(C_{total} \Delta \log D_p)$. The lower limit of the particle size collected on the back filter (D_p=0.01 µm) has been selected arbitrarily. Only results for compounds mainly associated to the particulate phase are considered in all this study. This concerns PAHs, OPAHs and NPAHs with at least 4 aromatic cycles (see Tables 1 and 2). Gas/particle partitioning of these compounds was determined experimentally by parallel measurements. These results and also those on atmospheric concentrations are presented and discussed in a companion paper (Albinet et al., 2007a).

3.2. PAH, OPAH and NPAH concentrations in the different size classes

Fig. 1 presents the average PAH, OPAH and NPAH fractional contents in the particle size classes according to sampling site and season (the compounds taken into account are listed in Tables 1 and 2).

In the winter period, about 90% of the PAHs, OPAHs and NPAHs were associated to the fine particles (D_p < 1.3 µm). This fraction was even higher for the PAH derivatives and could reach a value of 99% on average for the NPAHs. Moreover, the fractions of OPAHs (≈ 56%) and NPAHs (≈ 63%) associated with the finest particles (D_p < 0.39 µm) were significantly greater than for the PAHs (≈ 45%). This result is an important information regarding the risk assessment. Indeed, the more toxic OPAHs and NPAHs can also penetrate deeper into the organism.

In the summer period, the percentages associated to fine particles were lower than in winter accounting for about 80% for PAHs and OPAHs, and 60% for NPAHs. Size distributions of PAHs and OPAHs were similar and the percentage of compounds present on the finest aerosol fraction (<0.39 µm) was greater than in the winter period (excepted at M1 for the OPAHs) and ranged from 45 to 64%. By contrast the NPAH percentage on the back up filter (D_p <0.39 µm) was lower and ranged from 15 to 41%. Moreover, an important contribution to NPAH was provided by large (> 1.3 µm) particles.

3.3. Particle size distributions of PAHs

In the winter period, despite different sampling site characteristics (traffic, suburban, rural), geometric mean diameter (GMD) values were similar at all sites and ranged from 0.42 to 0.83 µm (Table 1). Additionally, geometric standard deviations (σ_g) of the GMDs were similar for all the sampling sites indicating a similar mass size distribution of these compounds. Fig. 2 and 3 show for the Chamonix and the Maurienne sampling sites, respectively, the weekly average normalized particle size distribution $\Delta C/(C_{total}\ \Delta \log\ D_p)$ of the high molecular weight PAHs (from

benz[a]anthracene to indeno[1,2,3,c,d]pyrene; see Table 1). The error bars indicate the standard deviation from the weekly average particle size distribution. The PAH distributions with particle size were quite similar at all sites in winter and with few exceptions in summer (C2 and M3, heavy compounds: see Table 2). The PAH mode was shifted to the ultra-fine particles (D_p < 0.2 µm) (Fig. 2 and 3). Unfortunately a detailed analysis of this size range (around 0.2 µm) was not possible. Size distributions of PAHs were broader in the summer (higher σ_g values) notably at the rural site M1. There the fraction of PAH associated to particles > 1.3 µm was more important.

3.4. Particle size distributions of OPAHs

During the winter campaign, GMD (< 1 µm), σg values and particle size distributions for OPAHs were similar to those of PAHs of similar molecular weights (228 and 252 g mol^{-1}) (Table 1). No differences of size distribution were observed between the OPAH congeners.

Similar features were observed for OPAHs in summer in the Cv, except for benzanthrone (GMD ≈ 0.80 µm and D_p = 2.75 µm at C1 (Table 2, Fig. 2 and 3). In the same period, at M1 the three OPAHs with MW = 230 g mol^{-1} presented GMDs > 1 µm, and benzanthrone GMD ≈ 2.3 µm. At the M3 site, the OPAH size distributions were identical in both seasons, while all of σ_g values were significantly higher at M1, concurrently with the existence of a secondary mode in the super micrometer particle range (Fig. 2 and 3).

3.5. Particle size distributions of NPAHs

In the winter period, GMD values for NPAHs were the lowest of all the compound families analyzed in this study ranged 0.25-0.85 µm (Table 1). Additionally, σ_g values were the lowest among all the compounds (1.00-2.85 µm) indicating a mass size distribution quite stable during this

season. Size distributions of NPAHs were unimodal, generally centred at D_p=0.85 µm (Fig 2 and 3) in all site, and at $D_p \approx 0.2$ µm for C1 and C2 (Table 2).

During the summer campaign, the situation was more complex. Unlike PAHs and OPAHs, GMD and σg of NPAHs were higher than in winter at all sampling sites (Table 2) and generally GMD values were lower than 1 µm. In the Cv (C1 and C2) NPAHs present globally unimodal size distributions centred at D_p = 0.85 µm (Fig. 2) but with some exceptions at C1 where the GMDs were equal to 0.2 for 6-nitrochrysene and 1,8-dinitropyrene, and 2.75 µm for 2+3-nitrofluoranthene. At this site, some NPAHs present bimodal size distributions (2-nitropyrene, modes at 0.85 and 27.1 µm; 6-nitrobenzo[a]pyrene, modes at 0.2 µm 2.75 µm). In the Mv, NPAH size distributions were all unimodal and globally centred at 2.75 µm (Fig. 3). At the rural site M1, half GMD values (mode at 2.75 µm) were larger than 1 µm whilst the others were very low and in the same order as in winter (about 0.3 µm: mode at 0.85 µm). Finally, at all sampling sites, the NPAH summer super micrometer fraction (> 1.3 µm) was largely more important than in winter.

4. Discussion

In general, particle size distribution of organic compounds is influenced by vapour pressure, and adsorption/absorption affinity of compounds, atmospheric processes, as well as the emission sources (Allen et al., 1996; Venkataraman and Friedlander, 1994; Venkataraman et al., 1999). Fine particles are mainly attributed to emissions from combustion processes and secondary reactions in the atmosphere, while coarse particles arise mainly from non-combustion processes, such as resuspension of surface dust and soil particles by wind action. Also, after their emission, semi-volatile organic compounds associated with fine particles could migrate during transport from fine to large particles by revolatilisation and sorption processes (Allen et al., 1996; Allen et al., 1997; Venkataraman et al., 1999). The rate of this flux is directly related to the gas phase concentration of

these compounds. Lower molecular weight compounds have higher vapour pressures, higher concentrations in the gas phase, higher diffusivities and, therefore could readily shift toward larger particle size. The high molecular weight compounds have generally much lower vapour pressures, and the characteristic time for this partitioning process is much greater (Allen et al., 1996; Offenberg and Baker, 1999).

PAHs are mainly emitted into the atmosphere from combustion sources, and removed by atmospheric wet and dry deposition and by photolysis and chemical reactions (Finlayson-Pitts and Pitts Jr, 2000). These is in agreement with our findings, as well as with studies conducted elsewhere (Aceves and Grimalt, 1993; Allen et al., 1996; Bi et al., 2005; Miguel et al., 2004; Van Vaeck and Van Cauwenberghe, 1978; Van Vaeck et al., 1979; Venkataraman and Friedlander, 1994) which report that PAHs and their derivatives are mainly associated (60-90%) with the fine aerosol fraction (D_p < 1.3 μm). The larger fraction of PAHs, OPAHs and NPAHs associated to coarse particles in summer seem to be in agreement with the association of these compounds to particulate following recondensation after volatilization/gas-phase emission.

Similarly, volatilization/recondensation seems to account for the high GMD values observed at M1 (rural), overall for low-MW PAHs.

Despite the evidence of secondary formation of NPAHs at site M1 during the summer period (Albinet et al., 2007a), no direct link can be established between the primary or secondary origin of these compounds and the GMD value variations observed at this site. GMD values of secondary NPAH compounds such as 2-nitropyrene and 2+3-nitropyrene were quite similar those of primary NPAH 1-nitropyrene. The size distributions of these two secondary compounds were unimodal and slightly shifted to fine particles (Fig. 4).

Then, mass transfer of PAHs, OPAHs and NPAHs from fine to large particles during aerosol ageing could explain the size distribution shifted to larger particles observed at the rural site M1.

The size distribution of PAHs, NPAHs and OPAHs revealed the existence of a second mode in the super micrometer particle size range in summer (Fig. 2 and 3). Similar evidence was reported (Jaffrezo et al., 2005) for elemental and organic carbon (EC and OC) during the same sampling campaigns at sites C1 and M2 (an other site in Mv). During the winter season, it was mixed and aged with possibility of adsorbing of gaseous organic compounds at the surface of pre-existing crustal particles.

By contrast, in summer period, NPAH portions in the super micrometer particles were more important than those of PAHs and OPAHs. The different behaviour is not well understood.

Like PAHs, OPAHs and NPAHs emitted by combustion sources are primarily associated with fine particles and secondary NPAHs (equally OPAHs) formed by gas phase reaction are transferred to the finest particles because of their greater specific surface. Based on our results, primary or secondary origins of the organic compounds do not seem to take a part in the difference of particle size distributions observed between the classes of compounds.

Moreover, the differences of vapour pressures do not also explain the larger NPAH fractions in the super micrometer size range. NPAH, PAH and OPAH vapour pressures are comparable for similar molecular weight. For instance, the vapour pressure of nitropyrene isomers (MW=247, vp = 4.4×10^{-6} Pa) can be compared to the one of benzo[a]pyrene (MW = 252, vp = 6.9×10^{-7} Pa) and the one of 6-nitrobenzo[a]pyrene (MW = 297, vp = 2.9×10^{-9} Pa) with that of coronene (MW = 300, vp = 1.9×10^{-10} Pa) (Yaffe et al., 2001). The vapour pressure at 25°C of benzanthrone (MW = 230) is 2.0×10^{-5} Pa and can be compared with the one of benz[a]anthracene and chrysene (MW = 252, vp = 2.7×10^{-5} Pa and 1.2×10^{-6} Pa) (De Kruif, 1980; Sonnefeld et al., 1983).

Finally, only a difference of chemical affinities of the organic compounds with the super micrometer fraction of the aerosol could explain the notable differences of size distributions of the

NPAHs, OPAHs and PAHs, but the phenomenon is not yet well understood and remains to be fully investigated.

5. Conclusion

The size distributions of the concentrations of PAHs, OPAHs and NPAHs presented large variations between winter and summer, and between traffic, suburban and rural sites. In general, at all sites and during both seasons, these compounds were mainly associated (60-90%) with fine particles (D_p < 1.3 µm) in agreement with their emission processes (primary and/or secondary). Mass transfer of organic compounds from fine to larger particles during aerosol ageing by this process could explain in the shift in size distribution to the larger particles observed at the rural site. At all the samplings sites, PAH, OPAH and NPAH particle size distributions were unimodal with a mode centred at about 0.85 µm during the winter period. In summer, similar size distribution was observed for all categories of compounds in the Cv. In the Mv, only NPAHs presented a shifted unimodal size distribution with a mode at D_p = 2.75 µm. PAH, OPAH and NPAH super micrometer fractions were significantly larger in summer than in winter for the majority of the sampling sites suggesting the existence of a second mode in the super micrometer particle size range in this season.

In summer, NPAHs were associated to a greater degree with the super micrometer fraction of the aerosol than the other categories of compounds. Neither their possible secondary origin nor a difference of vapour pressure could explain such differences. Only a difference of chemical affinity could explain it but this hypothesis needs further investigations to be understood.

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References

Aceves, M. and Grimalt, J. O., 1993. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. Environmental Science & Technology 27, 2896-2908.

Albinet, A.,Leoz-Garziandia, E.,Budzinski, H. and ViIlenave, E., 2006. Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. Journal of Chromatography A 1121, 106-113.

Albinet, A.,Leoz-Garziandia, E.,Budzinski, H. and Villenave, E., 2007a. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys. Part 1: Concentrations, sources and gas/particle partitioning. Atmospheric Environment (accepted for publication).

Albinet, A.,Leoz-Garziandia, E.,Budzinski, H. and Villenave, E., 2007b. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. Science of the Total Environment 384, 280-292.

Allen, J. O.,Dookeran, N. M.,Smith, K. A.,Sarofim, A. F.,Taghizadeh, K. and Lafleur, A. L., 1996. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts. Environmental Science & Technology 30, 1023.

Allen, J. O.,Dookeran, N. M.,Taghizadeh, K.,Lafleur, A. L.,Smith, K. A. and Sarofim, A. F., 1997. Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environmental Science & Technology 31, 2064-2070.

Arey, J.,Zielinska, B.,Atkinson, R.,Winer, A. M.,Ramdhal, T. and Pitts Jr, J. N., 1986. The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x. Atmospheric Environment 20, 2239-2345.

Atkinson, R.,Aschmann, S. M.,Arey, J. and Carter, P. L., 1989. Formation of ring-retaining products from the OH radical-initiated reactions of benzene and toluene. International Journal of Chemical Kinetics 21, 801-827.

Atkinson, R.,Arey, J.,Zielinska, B. and Aschmann, S. M., 1990. Kinetics and nitro-products of gas-phase OH and NO_3 radical-initiated reactions of naphthalene, fluoranthene and pyrene. International Journal of Chemical Kinetics 22, 999-1014.

Barbas, J. T.,Sigman, M. E. and Dabestani, R., 1996. Photochemical oxidation of phenanthrene sorbed on silica gel. Environmental Science and Technology 30, 1776-1780.

Bi, X.,Sheng, G.,Peng, P. a.,Chen, Y. and Fu, J., 2005. Size distribution of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of Guangzhou, China. Atmospheric Environment 39, 477-487.

Brulfert, G.,Chemel, C.,Chaxel, E. and Chollet, J.-P., 2005. Modelling photochemistry in alpine valleys. Atmospheric Chemistry and Physics.

Cecinato, A.,Marino, F.,Di Filippo, P.,Lepore, L. and Possanzini, M., 1999. Distribution of n-alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear aromatic hydrocarbons

between the fine and coarse fractions of inhalable atmospheric particulates. Journal of Chromatography A 846, 255-264.

De Kruif, C. G., 1980. Enthalpies of sublimation and vapour pressures of 11 polycyclic hydrocarbons. Journal of Chemical Thermodynamics 12, 243-248.

Durant, J. L.,Busby Jr, W. F.,Lafleur, A. L.,Penman, B. W. and Crespi, C. L., 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutation Research-Genetic Toxicology 371, 123-157.

Durant, J. L.,Lafleur, A. L.,Plummer, E. F.,Taghizadeh, K.,Busby, W. F. and Thilly, W. G., 1998. Human lymphoblast mutagens in urban airborne particles. Environmental Science & Technology 32, 1894-1906.

Environmental Health Criteria (EHC) 229, 2003. Selected nitro- and nitro-oxy-polycyclic aromatic hydrocarbons. WHO Library: http://whqlibdoc.who.int/ehc/WHO_EHC_229.pdf.

Finlayson-Pitts, B. J. and Pitts Jr, J. N., 2000. Chemistry of the upper and lower atmosphere. Wiley-Interscience: 969 p.

Hannigan, M. P.,Cass, G. R.,Penman, B. W.,Crespi, C. L.,Lafleur, A. L.,Busby Jr, W. F.,Thilly, W. G. and Simoneit, B. R. T., 1998. Bioassay-Directed Chemical Analysis of Los Angeles Airborne Particulate Matter Using a Human Cell Mutagenicity Assay. Environmental Science & Technology 32, 3502-3514.

Hayakawa, K.,Kawaguchi, Y.,Murahashi, T. and Miyazaki, M., 1995. Distributions of nitropyrenes and mutagenicity in airborne particulates collected with an Andersen sampler. Mutation Research 348, 57-61.

Helmig, D. and Harger, W. P., 1994. OH radical-initiated gas-phase reaction products of phenanthrene. The Science of the Total Environment 148, 11-21.

Jaffrezo, J.-L.,Aymoz, G. and Cozic, J., 2005. Size distribution of EC and OC in the aerosol of Alpines valleys during summer and winter. Atmospheric Chemistry and Physics 5, 2915-2925.

Jinhui, X. and Lee, F. S. C., 2000. Quantification of nitrated polynuclear aromatic hydrocarbons in atmospheric particulate matter. Analytica Chimica Acta 416, 111-115.

Kawanaka, Y.,Matsumoto, E.,Sakamoto, K.,Wang, N. and Yun, S.-J., 2004. Size distributions of mutagenic compounds and mutagenicity in atmospheric particulate matter collected with a low-pressure cascade impactor. Atmospheric Environment 38, 2125-2132.

Lewtas, J.,Nishioka, M. and Peterson, B., 1990. Bioassay directed fractionation of the organic extract of SRM 1649 urban air particulate and ambient matter. International Journal of Environmental Analytical Chemistry 39, 245-256.

Miguel, A. H.,Eiguren-Fernandez, A.,Jaques, P. A.,Froines, J. R.,Grant, B. L.,Mayo, P. R. and Sioutas, C., 2004. Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California. Atmospheric Environment 38, 3241-3251.

Offenberg, J. H. and Baker, J. E., 1999. Aerosol Size Distributions of Polycyclic Aromatic Hydrocarbons in Urban and Over-Water Atmospheres. Environmental Science & Technology 33, 3324-3331.

Pedersen, D. U.,Durant, J. L.,Penman, B. W.,Crespi, C. L.,Hemond, H. F.,Lafleur, A. L. and Cass, G. R., 2004. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. Environmental Science & Technology 38, 682-689.

Pedersen, D. U.,Durant, J. L.,Taghizadeh, K.,Hemond, H. F.,Lafleur, A. L. and Cass, G. R., 2005. Human cell mutagens in respirable airborne particles from the Northeastern United States. 2. Quantification of mutagens and other organic compounds. Environmental Science & Technology 39, 9547-9560.

Perraudin, E.,Budzinski, H. and Villenave, E., 2007. Identification and quantification of primary ozonation products of phenanthrene and anthracene adsorbed on silica particles. Atmospheric Environment in press.

Sasaki, J.,Aschmann, S. M.,Kwok, E. S. C.,Atkinson, R. and Arey, J., 1997. Products of the Gas-Phase OH and NO_3 Radical-Initiated Reactions of Naphthalene. Environmental Science & Technology 31, 3173-3179.

Schnelle-Kreis, J.,Gebefugi, I.,Welzl, G.,Jaensch, T. and Kettrup, A., 2001. Occurrence of particle-associated polycyclic aromatic compounds in ambient air of the city of Munich. Atmospheric Environment 35, 71-81.

Schuetzle, D., 1983. Sampling of vehicle emissions for chemical analysis and biological testing. Environmental Health Perspectives 47, 65-80.

Sonnefeld, W. J.,Zoller, W. H. and May, W. E., 1983. Dynamic coupled-column liquid chromatographic determination of ambient temperature vapor pressures of polynuclear aromatic hydrocarbons. Analytical Chemistry 55, 275-280.

Van Vaeck, L. and Van Cauwenberghe, K., 1978. Cascade impactor measurements of size distribution of the major classes of organic pollutants in atmospheric particulate matter. Atmospheric Environment 12, 2229-2239.

Van Vaeck, L.,Broddin, G. and Van Cauwenberghe, K., 1979. Differences in particle size distribution of major organic pollutants in ambient aerosols in urban, rural and seashore areas. Environmental Science & Technology 13, 1494-1502.

Venkataraman, C. and Friedlander, S. K., 1994. Size distribution of polycyclic aromatic hydrocarbons and elemental carbon. 2. Ambient measurements and effects of atmospheric processes. Environmental Science & Technology 28, 563-572.

Venkataraman, C.,Thomas, S. and Kulkarni, P., 1999. Size distributions of polycyclic aromatic hydrocarbons-gas/particle partitioning to urban aerosols. Journal of Aerosol Science 30, 759-770.

Yaffe, D.,Cohen, Y.,Arey, J. and Grosovsky, A. J., 2001. Multimedia analysis of PAHs and nitro-PAH daughter products in the Los Angeles basin. Risk Analysis 21, 275-294.

Table 1

Arithmetic averages of the geometric mean diameters (GMD) and of geometric standard deviations (σ_g) of individual PAHs, NPAHs and OPAHs at all sampling sites during the winter 2002-2003 campaign (n=7)

Compounds	Molecular weight (g mol^{-1})	GMD C1 (µm)	CV[a] C1 (%)	σ_g C1 (µm)	GMD C2 (µm)	CV[a] C2 (%)	σ_g C2 (µm)	GMD M1 (µm)	CV[a] M1 (%)	σ_g M1 (µm)	GMD M3 (µm)	CV[a] M3 (%)	σ_g M3 (µm)
PAHs													
Benz[a]anthracene	228	0.50	28	2.74	0.59	17	2.62	0.56	9	2.77	0.58	23	2.83
Chrysene	228	0.52	20	2.93	0.60	18	2.82	0.53	14	2.92	0.57	24	3.18
Benzo[e]pyrene	252	0.43	15	2.62	0.51	16	2.51	0.54	25	2.36	0.56	30	2.68
Benzo[b]fluoranthene	252	0.50	20	2.85	0.58	19	2.66	0.53	17	2.78	0.57	24	3.03
Benzo[k]fluoranthene	252	0.50	21	2.83	0.59	17	2.68	0.55	16	2.74	0.56	22	2.96
Benzo[a]pyrene	252	0.51	26	2.59	0.61	22	2.50	0.60	19	2.52	0.60	26	2.74
Dibenz[a,h]anthracene	278	0.69	20	3.07	0.83	24	3.26	0.62	25	2.61	0.56	35	2.73
Benzo[g,h,i]perylene	276	0.42	14	2.99	0.49	20	2.96	0.54	17	2.79	0.54	27	3.12
Indeno[1,2,3,c,d]pyrene	276	0.47	21	2.94	0.56	19	2.86	0.57	18	2.82	0.58	22	3.00
OPAHs													
Benzo[a]fluorenone	230	0.43	24	2.61	0.49	20	2.49	0.44	6	2.99	0.66	62	3.46
Benzo[b]fluorenone	230	0.42	26	2.57	0.51	22	2.42	0.44	9	2.76	0.60	56	3.20
Benzanthrone	230	0.40	20	2.52	0.48	22	2.22	0.41	15	2.47	0.60	56	3.03
Benz[a]anthracene-7,12-dione	258	0.44	18	2.73	0.50	20	2.49	0.44	13	2.89	0.59	72	3.12
NPAHs													
2+3-Nitrofluoranthene	247	0.32	17	1.93	0.34	19	1.96	0.34	15	2.01	0.33	34	1.90
4-Nitropyrene	247	0.35	20	2.03	0.39	23	2.01	0.38	19	2.07	0.37	43	1.98
1-Nitropyrene	247	0.30	12	2.12	0.30	20	1.96	0.35	14	2.31	0.38	52	2.24
2-Nitropyrene	247	0.33	21	2.10	0.41	24	2.03	0.33	15	2.02	0.67	88	2.85
7-Nitrobenz[a]anthracene	273	0.25	16	1.62	0.29	20	1.77	0.33	21	1.93	0.36	45	2.00
6-Nitrochrysene	273	0.25	20	1.54	0.37	34	1.85	0.32	22	2.05	0.83	109	1.78
1,3-Dinitropyrene	292	0.41	26	2.01	0.84	102	1.78	0.47	27	1.96	0.49	31	2.27
1,6-Dinitropyrene	292	0.25	30	1.34	nd[b]	-	-	0.31	20	1.00	0.20	30	1.00
1,8-Dinitropyrene	292	0.37	22	2.03	0.43	22	2.05	0.43	21	2.03	0.46	29	2.20
6-Nitrobenzo[a]pyrene	297	0.31	16	2.24	0.35	21	2.13	0.36	17	2.31	0.79	121	1.95

[a] Coefficient of Variation = standard deviation/mean.

[b] not detected

Table 2

Arithmetic averages of the geometric mean diameters (GMD) and of geometric standard deviations (σ_g) of individual PAHs, NPAHs and OPAHs at all sampling sites during the summer 2003 campaign (n=7)

Compounds	Molecular weight (g mol^{-1})	GMD C1 (µm)	CV[a] C1 (%)	σ_g C1 (µm)	GMD C2 (µm)	CV[a] C2 (%)	σ_g C2 (µm)	GMD M1 (µm)	CV[a] M1 (%)	σ_g M1 (µm)	GMD M3 (µm)	CV[a] M3 (%)	σ_g M3 (µm)
PAHs													
Benz[a]anthracene	228	0.47	22	3.12	0.38	11	3.17	1.40	64	5.14	0.56	16	2.90
Chrysene	228	0.50	17	3.19	0.42	13	3.11	0.86	65	4.50	0.44	17	2.73
Benzo[e]pyrene	252	0.48	20	3.38	0.48	16	3.85	0.74	54	4.03	0.45	19	2.76
Benzo[b]fluoranthene	252	0.53	21	3.09	0.44	15	3.11	0.70	43	4.14	0.41	19	2.68
Benzo[k]fluoranthene	252	0.54	25	3.05	0.43	15	2.97	0.80	43	4.46	0.40	20	2.55
Benzo[a]pyrene	252	0.53	33	3.26	0.44	15	3.36	0.78	38	4.44	0.41	14	2.65
Dibenz[a,h]anthracene	278	0.77	96	2.34	0.52	55	3.16	0.75	39	4.77	0.53	42	2.95
Benzo[g,h,i]perylene	276	0.49	21	3.61	0.39	18	3.44	0.65	25	4.25	0.39	24	2.43
Indeno[1,2,3,c,d]pyrene	276	0.46	26	3.08	0.37	15	2.99	0.63	21	4.15	0.36	27	2.41
Coronene	300	0.53	26	4.36	0.44	23	4.19	0.59	38	4.00	0.34	13	2.50
OPAHs													
Benzo[a]fluorenone	230	0.46	19	3.18	0.55	33	3.80	1.14	35	4.54	0.53	19	3.92
Benzo[b]fluorenone	230	0.51	23	3.34	0.53	30	3.57	1.27	34	4.55	0.56	12	3.66
Benzanthrone	230	0.80	66	3.12	0.44	40	2.82	2.34	42	4.25	0.51	33	2.92
Benz[a]anthracene-7,12-dione	258	0.44	20	2.95	0.50	33	3.39	0.65	30	3.74	0.44	11	3.53
NPAHs													
2+3-Nitrofluoranthene	247	0.67	29	2.50	0.69	18	2.52	1.20	45	3.40	0.64	32	2.44
4-Nitropyrene	247	0.54	48	2.74	0.48	64	3.48	0.27	40	1.33	1.00	50	3.28
1-Nitropyrene	247	0.42	33	2.53	0.71	35	3.00	1.03	12	3.39	0.79	14	2.84
2-Nitropyrene	247	0.79	56	2.05	1.21	34	2.12	1.47	45	2.71	1.69	37	2.41
7-Nitrobenz[a]anthracene	273	0.39	79	1.57	0.49	120	1.71	0.31	24	2.47	0.66	43	2.65
6-Nitrochrysene	273	nd[b]	-	-	1.30	25	1.33	0.34	46	1.52	6.76	168	1.14
1,3-Dinitropyrene	292	0.22	20	1.11	1.85	67	1.00	4.54	91	2.43	nd	-	-
1,6-Dinitropyrene	292	nd	-	-	nd	-	-	nd	-	-	nd	-	-
1,8-Dinitropyrene	292	0.21	15	1.14	0.53	72	2.89	0.38	74	1.28	0.54	67	2.26
6-Nitrobenzo[a]pyrene	297	0.69	173	1.05	0.90	128	1.17	1.74	59	3.87	0.91	67	2.14

[a] Coefficient of Variation = standard deviation/mean.

[b] not detected

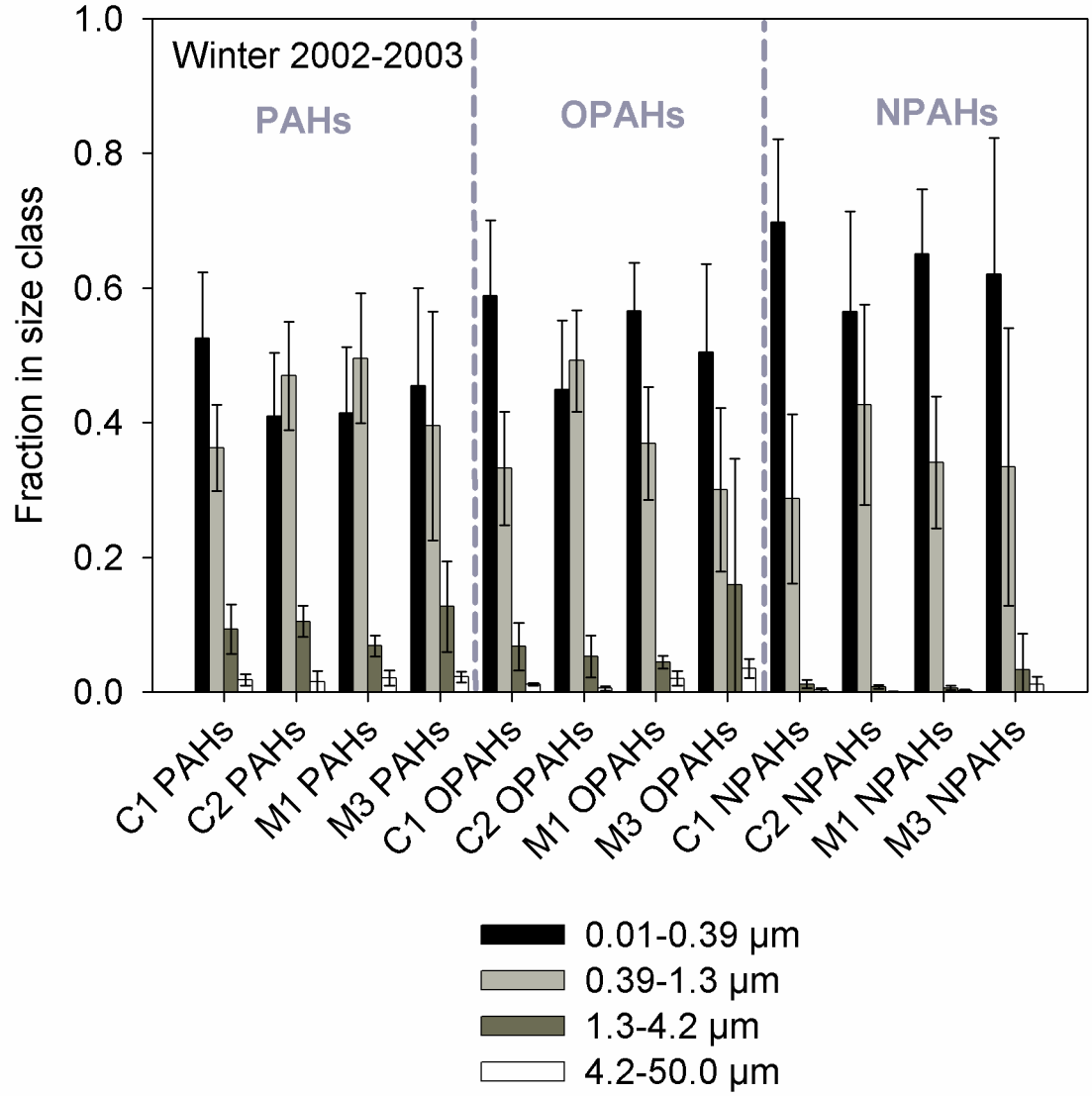
Figure Captions

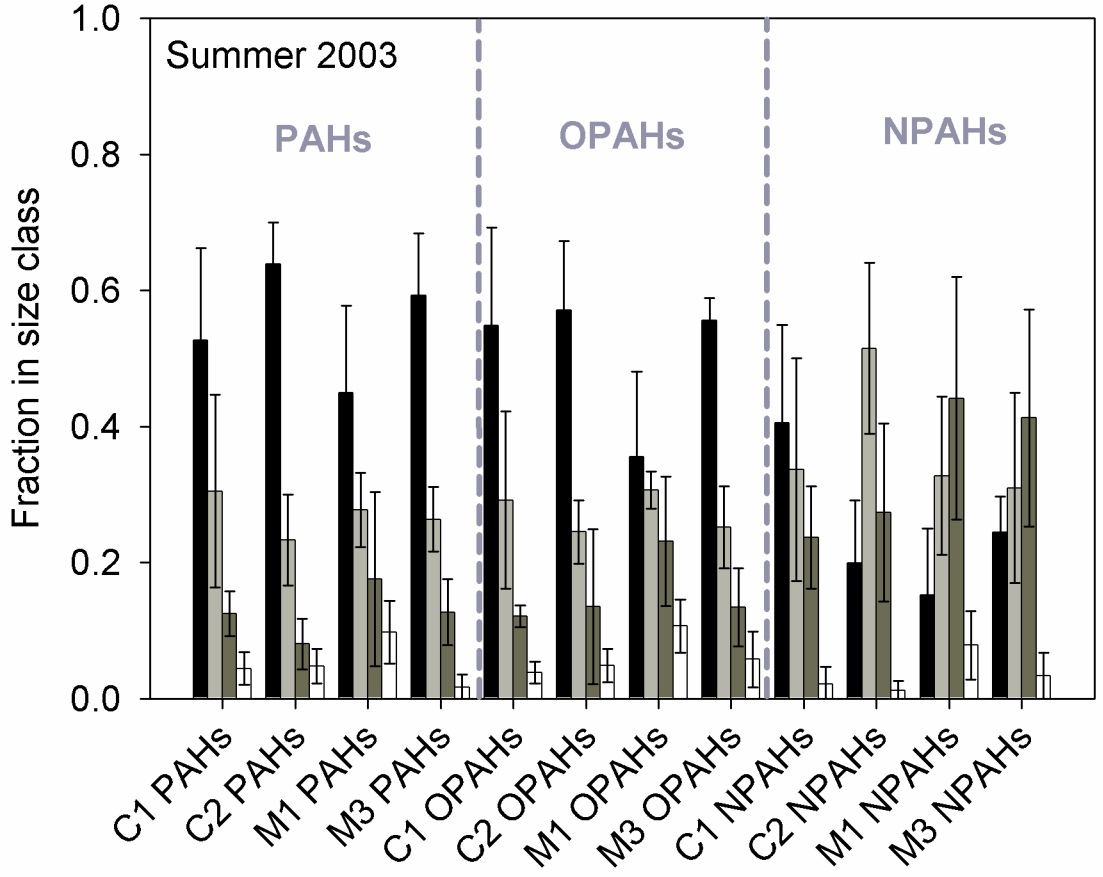
Fig. 1. Average PAH, OPAH and NPAH concentration fractions in the different particle size classes at each sampling site during the winter 2002-2003 and the summer 2003 campaigns. The error bars show the standard deviation from the weekly average (n=7).

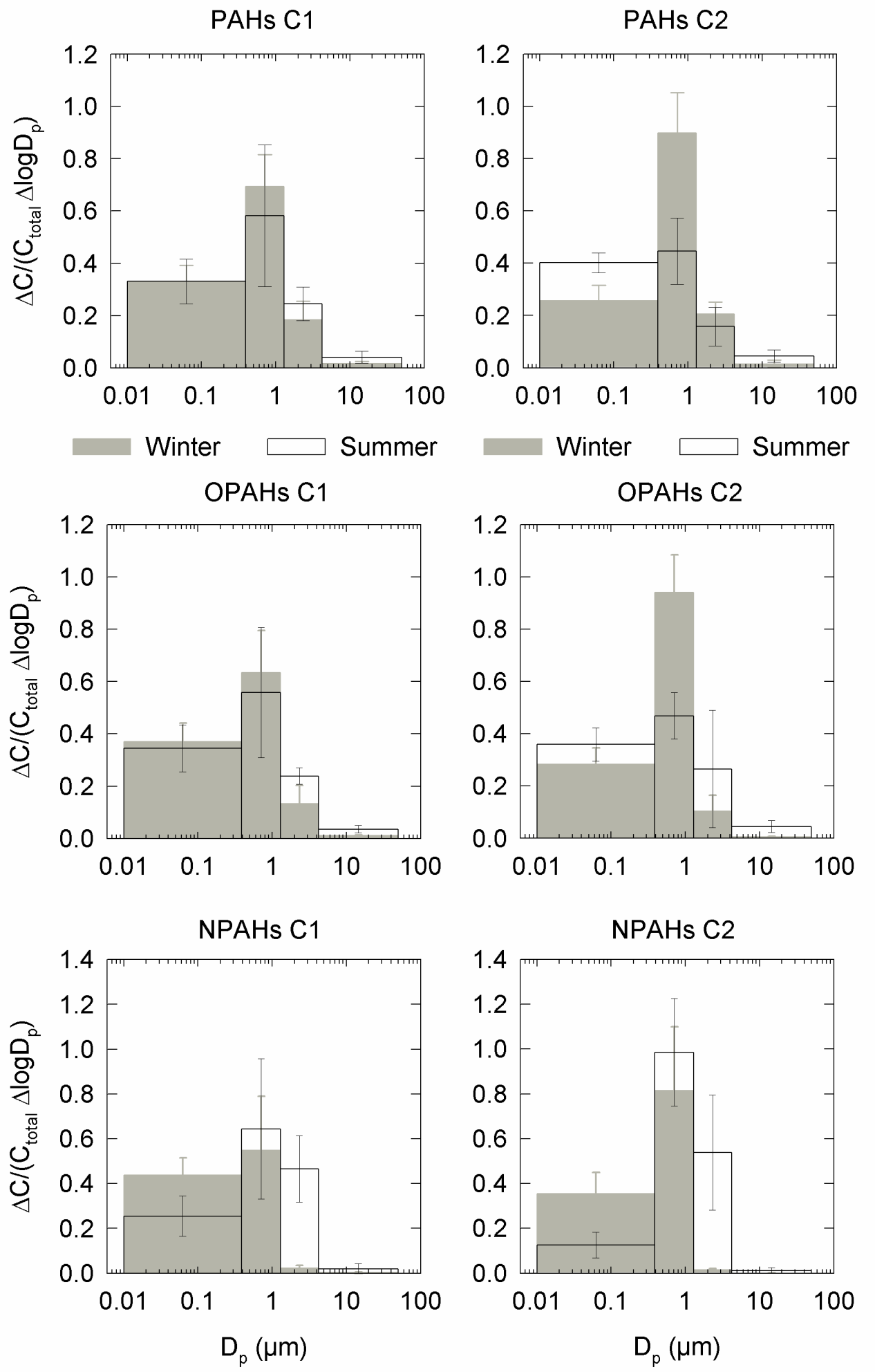
Fig. 2. Particle size distributions of PAHs, OPAHs and NPAHs at sites C1 and C2 in the Chamonix valley during the winter 2002-2003 and the summer 2003 sampling campaigns. The error bars show the standard deviation from the weekly average size distribution (n=7).

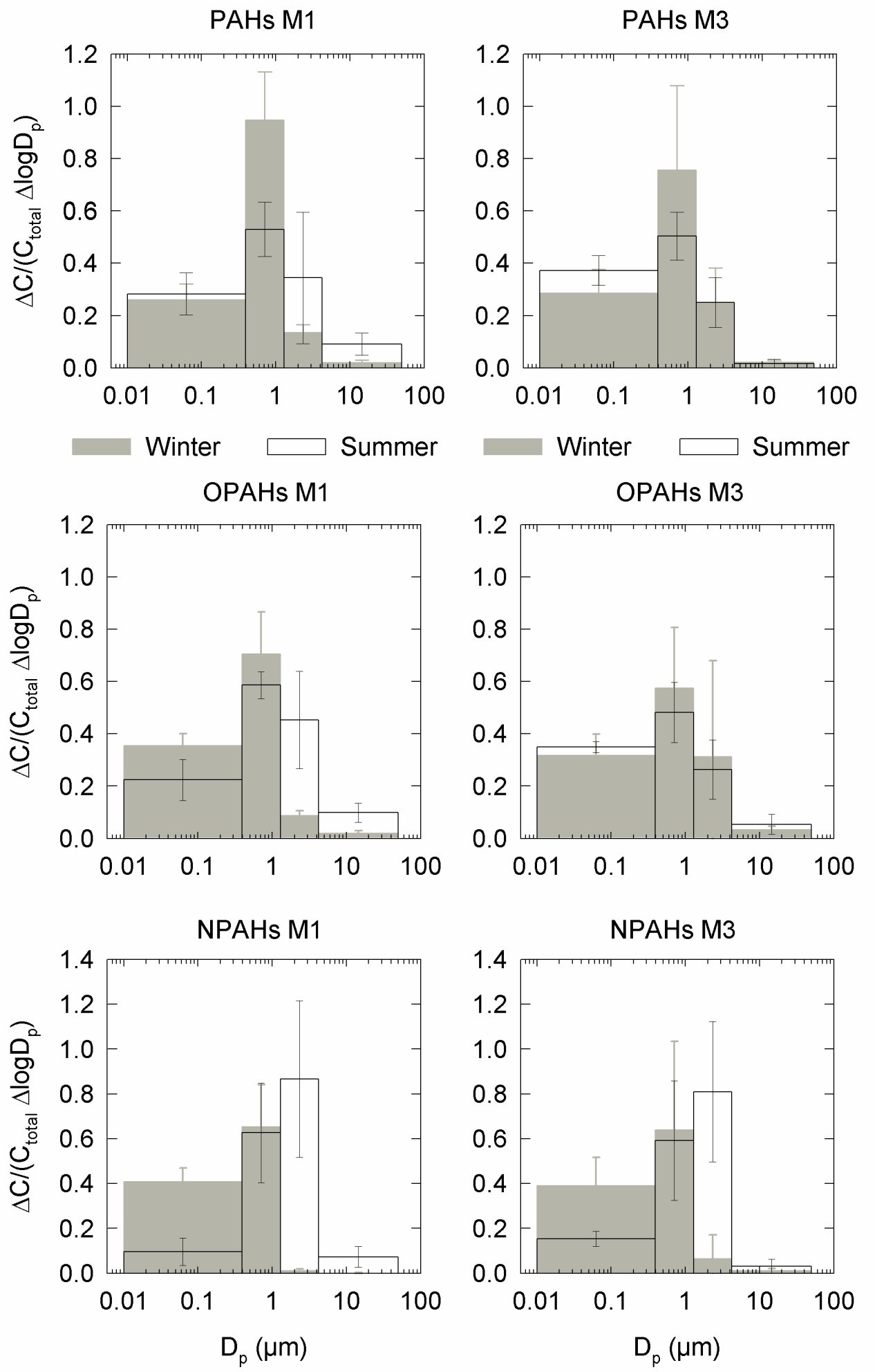
Fig. 3. Particle size distributions of PAHs, OPAHs and NPAHs at sites M1 and M2 in the Maurienne valley during the winter 2002-2003 and the summer 2003 sampling campaigns. The error bars show the standard deviation from the weekly average size distribution (n=7).

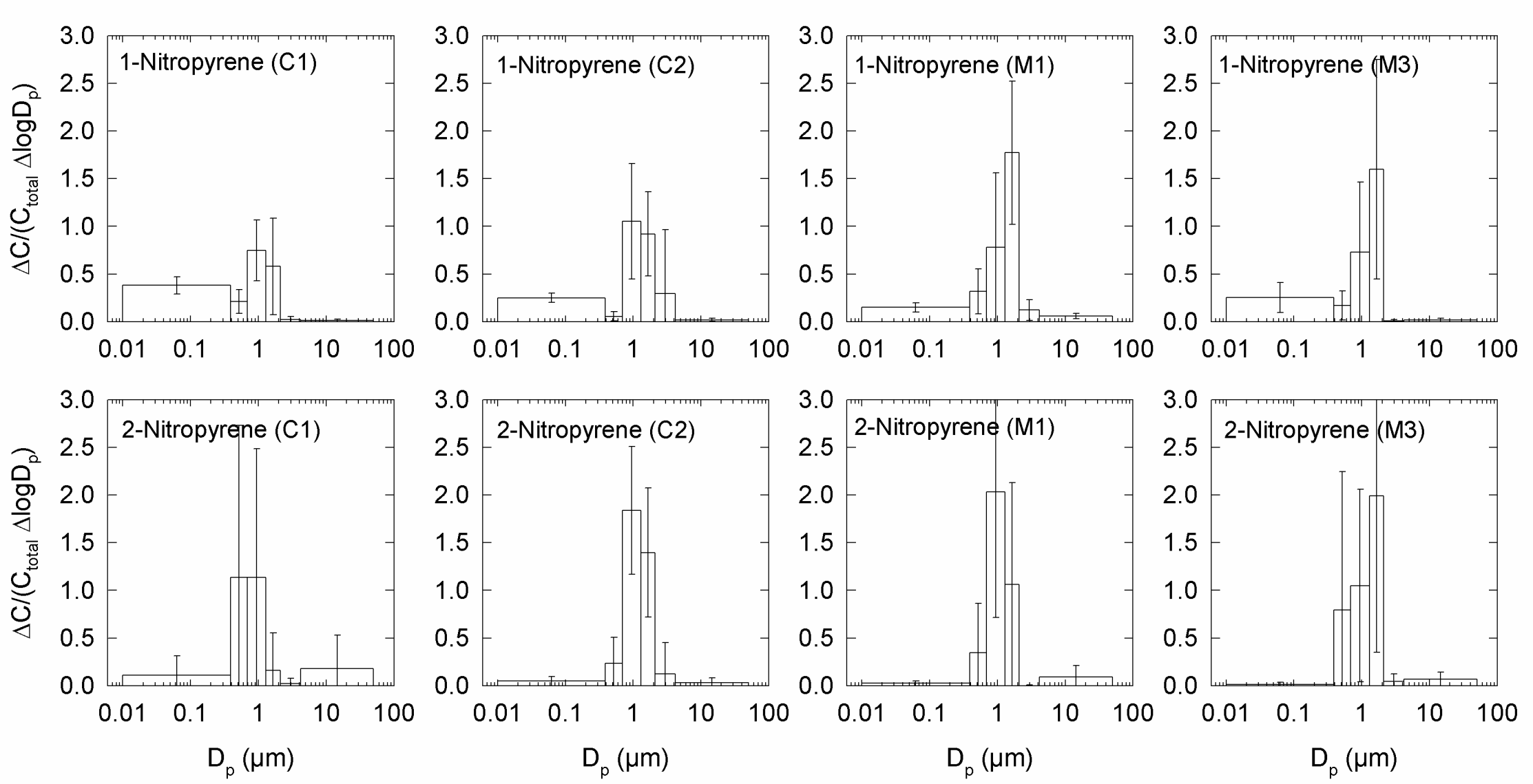
Fig. 4. Particle size distributions of 1- and 2-nitropyrene at the fourth instrumented sites (C1, C2, M1 and M3) during the summer 2003 sampling campaign. The error bars show the standard deviation from the weekly average size distribution (n=7).


Winter 2002-2003
PAHs
OPAHs
NPAHs
Fraction in size class
1.0
0.8
0.6
0.4
0.2
0.0
C1 PAHs
C2 PAHs
M1 PAHs
M3 PAHs
C1 OPAHs
C2 OPAHs
M1 OPAHs
M3 OPAHs
C1 NPAHs
C2 NPAHs
M1 NPAHs
M3 NPAHs
0.01-0.39 µm
0.39-1.3 µm
1.3-4.2 µm
4.2-50.0 µm


Summer 2003
PAHs
OPAHs
NPAHs
Fraction in size class
1.0
0.8
0.6
0.4
0.2
0.0
C1 PAHs
C2 PAHs
M1 PAHs
M3 PAHs
C1 OPAHs
C2 OPAHs
M1 OPAHs
M3 OPAHs
C1 NPAHs
C2 NPAHs
M1 NPAHs
M3 NPAHs


PAHs C1
PAHs C2
OPAHs C1
OPAHs C2
NPAHs C1
NPAHs C2
ΔC/(C_total ΔlogD_p)
D_p (μm)
Winter
Summer
0.01
0.1
1
10
100
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4


PAHs M1
PAHs M3
OPAHs M1
OPAHs M3
NPAHs M1
NPAHs M3
ΔC/(C_total ΔlogD_p)
D_p (μm)
Winter
Summer
0.01
0.1
1
10
100


1-Nitropyrene (C1)
1-Nitropyrene (C2)
1-Nitropyrene (M1)
1-Nitropyrene (M3)
2-Nitropyrene (C1)
2-Nitropyrene (C2)
2-Nitropyrene (M1)
2-Nitropyrene (M3)
ΔC/(C_total ΔlogD_p)
D_p (μm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0.01
0.1
1
10
100